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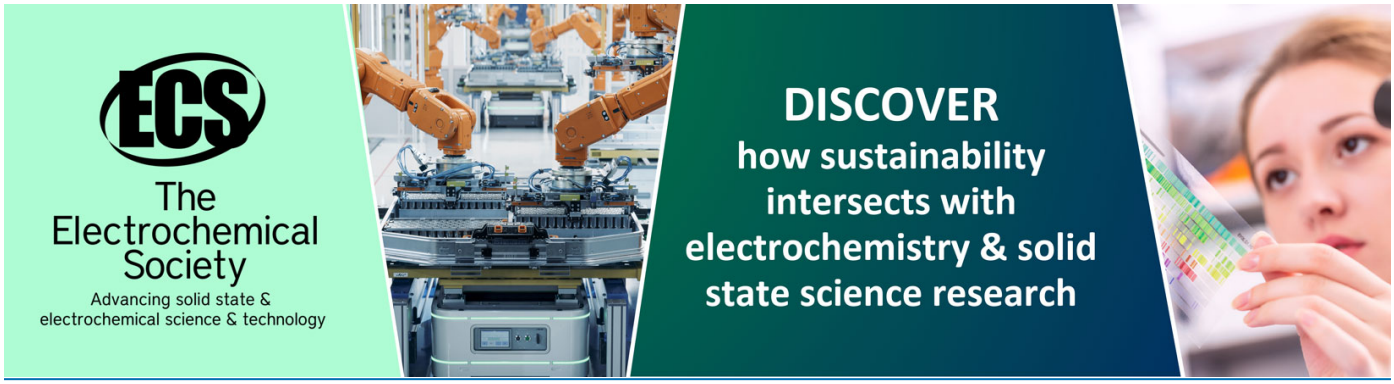

Structural properties and bonding characteristic of magnesium (Mg) doped zinc oxide (ZnO)

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Abstract. Structural properties and bonding characteristics of Mg doped ZnO by co-precipitation methods were characterized by using X-ray Diffraction (XRD) and Fourier Transforms Infrared (FTIR) spectroscopy. The analysis of FTIR showed peaks at 466.77 cm^{-1} and 451.31 cm^{-1} which correspond to the stretching of the oxygen bond in the ZnO structure and leads to defect formation by the oxygen atom detachment. This defect occupied by the Mg atom and proved by the widening of peak oxygen. The data XRD showed increasing the average size of ZnO crystal from 27.74 nm to 38.17 nm with the addition of 10% wt of Mg. These phenomena indicated agglomeration of the partial displacement of O^{2-} by Mg^{2+} in the MgZnO structure. This study showed simple methods to combine with Mg atom and ZnO to produce potential materials for catalytic applications.

1. Introduction

In the last decades, semiconductor materials, especially semiconductors II-VI, have attracted many researchers because of its various advantages such as non-expensive, easily synthesized, non-toxic, and many applications of nanoscale materials [1][2]. One type of this material is Zinc Oxide (ZnO) [2]. ZnO is a semiconductor with a band gap between 3.3 eV and binding energy 60 meV [1][3][4][5][6][7]. These characteristics are the reason applicated ZnO in the industry, namely photocatalytic, photodetector, energy storage, chemical sensing, nonlinear optics, magnetic semiconductor, ultraviolet/blue emission, including electronic optics and acoustic devices [1][2][3][5][7] Besides that, ZnO is materials that can be used for pollutant removal of industrial and domestic waste [4][8][9][10], which has low cost, intoxicate abundance, and high surface activity semiconductor [8].

In 2015 Klubnuan et al., Synthesized MgO/ZnO by hydrothermal method which requires high temperature and long-time processing step of 180ºC for 5 hours [12]. Similarly, Alhardan et al in 2017 also synthesized Magnesium Doping ZnO by hydrothermal method of a temperature of 95ºC for 6 hours [7]. In addition, Hu Yonghong et al in 2016 also succeeded in synthesizing Mg doping with ZnO using the one-pot method [13]. In some case, defecting can be occuring to atom bond. Point defects atom has two types namely Schottky defects and Frenkel defects which may be present in Mg doping ZnO nanoparticles as described by (Rao.et.al 2018). Based on the Frenkel defect using Krozer-Vink notation, the site occupied by the Zinc atom (Zn_i^x) together with an equivalent vacancy (V_{Zn}^x)

undergoes an ionization reaction to the Zn ion. Thus, vacancies at ZnO crystals are made by moving Zn^{2+} ions to the interstitial site.

In this study, ZnO doped with a metal element. ZnO has been doped with a Magnesium (Mg) to produce a material that has optimal on the photocatalytic process. In this study, we used the co-precipitation method which has a simple method, effective and efficient synthesis. The dopant variations used were 5% and 10% of Mg and the characterization by using Fourier Transform Infrared (FTIR) and X-ray Diffraction (XRD)

2. Experimental

2.1. Material

Zinc Chloride ($ZnCl_2$) 0.035 M (Merck), Sodium Hydroxide (NaOH) 0.070 M (Merck), Magnesium Chloride Hexahydrate ($MgCl_2.6H_2O$) (Merck), and Ethanol Pro Analysis 99.99% (JT. Backer).

2.2. Synthesis of Mg-ZnO

ZnO and Mg-doped ZnO nanoparticles (Mg: ZnO NPs) are prepared by hydrolysis of Zinc Chloride ($ZnCl_2$) and Sodium Hydroxide (NaOH). A solution 0.035 M $ZnCl_2$ dissolved on 50 ml ethanols and heating process of 65ºC for 30 minutes on a magnetic stirrer (600 rpm). Then the solution cool about room temperature. Synthesis Mg-ZnO starting with mixing $ZnCl_2$ with $MgCl_2.6H_2O$ (5% and 10% wt). 0.070 M of a solution of Sodium Hydroxide (NaOH) dissolved on 50 mL of ethanol at room temperature. This solution dripped into Zinc Chloride ($ZnCl_2$) solution and $ZnCl_2$ plus $MgCl_2.6H_2O$ respectively. The stirring process was continued for 60 minutes at 600 rpm at room temperature then centrifuged at 3000 rpm for 5 minutes to separate the ZnO from the supernatant for 3 times. After being centrifuged, the precipitate is dried at 80°C until dry then the powder is calcined at 600ºC for 2 hours [2]. It can result in a powder of ZnO and Mg-ZnO (5% and 10%).

2.3. Material Characterization

Crystallite size of the samples is determined using the X-ray diffraction (XRD) data. Diffraction pattern was collected on XRD spectroscopy (Shimadzu 7000) with CuKα radiation (λ=1,5405 amstrom) over the angular range $15^o \leq 2\theta \leq 80^o$, operation at 30 kV and 10 mA. Fourier transform infrared (FTIR) spectroscopy was carried out on an IRPrestige-21 FTIR spectrometer (Shimadzu Corp.) equipped with a bright ceramic light source, a KBr beamsplitter, and a deuterated triglycine sulfate doped with L-alanine (DLATGS) detector.

In the process of synthesis, two types of point defects viz., Schottky defects and Frenkel defects are possible to be present in ZnMgO nanoparticles, which can be explained by using Krozer-Vink notation. According to the Schottky defect, the Zn site void (V_{Zn}^x)) together with the Oxygen site vacuums (V_O^x) undergoes an ionization reaction so that the vacancy at ZnO Crystal is made to move oxygen ions to the crystal surface, as explained by (Rao.et. al 2018) in the equation below [13]:

$$Zn_{Zn}^x + O_O^x \leftrightarrow V_{Zn}'' + V_O^{\bullet\bullet} + (Zn_{Zn}^x)_{surface} + (O_o^x)_{surface} \qquad (1)$$

The average grain size (D) of the sample uses the Debye-Scherrer equation [14].

$$D = \frac{k\,\lambda}{B\cos\theta} \qquad (2)$$

Where, k is a constant (0.9), λ is the X-ray wavelength (0.154 nm), B is the full width at the maximum half, and θ is the Bragg angle.

3. Results and Discussion

3.1. FT-IR Spectrum

The FT-IR spectrum of ZnO and Mg-doped ZnO powders is shown in Figure 1, recorded from 4000 to 250 cm^{-1} wave number.

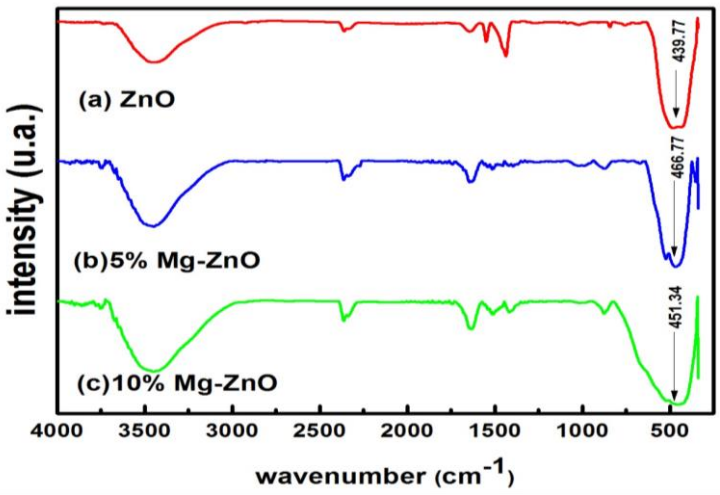

Figure 1. FTIR spectrum of ZnMgO nanoparticles

The FTIR spectrum for ZnO without doping (Fig. 1a) shows the absorption peaks associated with ZnO bonds stretching from a peak of 400 cm^{-1} to 500 cm^{-1}. This strong peak absorption at 439.77 cm^{-1} indicated Zn-O bond. The FTIR spectrum of 5% Mg-ZnO (Fig. 1b) shows that increasing absorption band compared to the peak of ZnO (Fig. 1a) at 439.77 cm^{-1} to 466.77 cm^{-1}. It indicates that Oxygen stretching from ZnO occupied by Mg to be ZnMgO. Likewise, 10% Mg-ZnO shows the position of oxygen which is stretching from ZnO. It caused Mg vacancies occupied so makes widening peaks of Mg-ZnO. This process due to 5% Mg-ZnO (Fig. 1b) but has a smaller width peak than 10% Mg-ZnO. the widening of peak indicated Mg combination of ZnO. It means that ZnMgO has characteristic to the application of catalytic.

3.2. X-RAY DIFFRACTION (XRD)

Figure 2 shows the XRD spectrum of ZnMgO nanoparticles. The XRD pattern shows the diffraction peaks of ZnO such as (0 0 2), (1 0 1), (1 0 3), (2 0 0), (2 0 1). This reflection plane shows that the prepared sample is ZnO structure and contains a phase in ZnO and Mg-doped ZnO samples. The relevant data in the XRD spectrum are presented in Table 1.

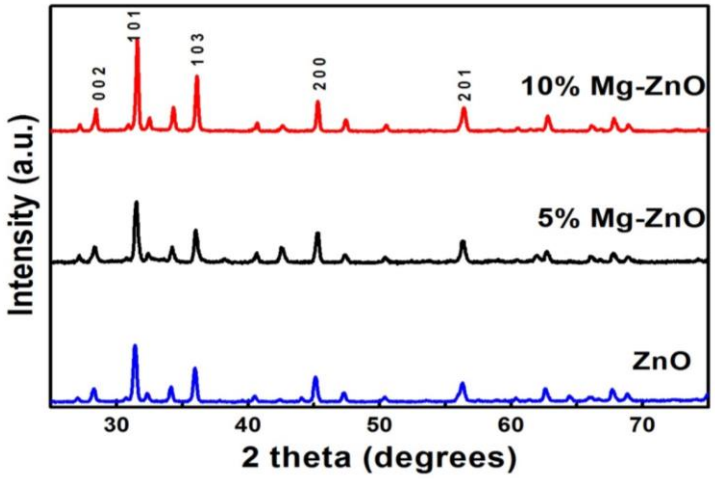

Figure 2. The XRD Spectrum of MgZnO nanoparticles

Based on Figure 2, addition magnesium effects increasing intensity of MgZnO at (0 0 2), (1 0 1), (1 0 3), (2 0 0), (2 0 1). It means that Mg suitable combine with ZnO. Without changing the crystal structure, Mg^{2+} ions have occupied Zn^{2+} ions and magnesium ions will affect interstitial zinc ion

concentrations and zinc vacancies and vacancies for oxygen. A very small shifting shown in addition to 5% Mg. While at the addition of 10% Mg shows the expansion of the diffraction peaks that are formed higher and shifting clearly visible.

Table 1. Data relevant to the XRD spectrum of MgZnO Nanoparticles

Sample	2θ	θ	cos θ	Wavelength λ (nm)	FWHM (deg)	FWHM (Radian)	Crystal Size (nm)	Average Crystal Size (nm)
ZnO	31.37	15.69	0.96	0.154	0.3155	0.0055	26.16	27.74
	35.93	17.96	0.95	0.154	0.2874	0.0050	29.06	
	45.09	22.55	0.92	0.154	0.3072	0.0054	28.00	
5% Mg-ZnO	31.47	15.73	0.96	0.154	0.299	0.0052	27.61	28.27
	45.24	22.62	0.92	0.154	0.2976	0.0052	28.92	
	36.00	18.00	0.95	0.154	0.2953	0.0052	28.29	
10% Mg-ZnO	31.55	15.77	0.96	0.154	0.2121	0.0037	38.92	38.17
	36.08	18.04	0.95	0.154	0.2289	0.0040	36.50	
	45.27	22.64	0.92	0.154	0.2202	0.0038	39.09	

The suitable combine of Mg and ZnO supported data on Table 1. In the ZnO sample, the average crystal size is 27.74 nm. After addition 5% Mg, the average size of Crystal increasing to be 28.27 nm while the addition of 10% Mg increases to 38.17 nm. Increasing of the average size of crystal MgZnO indicated the effect of Mg and it confirms the suitability of MgZnO for catalytic applications. This result shows that the method presented in this study is the simple way for the synthesis of semiconductor doped by alkaline metal for various applications.

4. Conclusion

ZnO and Mg doping ZnO successfully synthesized by co-precipitation method. In FTIR spectrum absorption has strong peaks at 439.20 cm^{-1} with stretching the vibration of Zn-O bonds. The ZnO vibration induced by Magnesium in the range of 451.34 cm^{-1} and 522.71 cm^{-1} observed in the sample that determines the microstructure changed by adding Magnesium to the Zinc Oxide lattice. Whereas the XRD results showed the average size on ZnO samples are 27.74 nm. The addition of 5% Mg and 10% Mg to ZnO changes the average size of Crystal are 28.27 nm and 38.17 nm respectively. It indicated that Mg suitable to combine with ZnO.

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